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The Chemical Compatibility of Thermoplastic Hose used in Umbilicals

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ABSTRACT

The effects of solvents and temperature on thermoplastic hose for umbilical service are reported in this paper. Accelerated ageing tests were undertaken and analysed by gravimetric, mechanical and calorimetric measurements. Water and methanol were found to cause physical degradation of the polymer, mainly at high temperatures, whereas xylene caused chemical degradation, which increased with increasing temperature.
The activation energy for the α-process within polyethylene (PE) was found to be 96.3 kJ mol^{-1} for un-aged PE and increased to 106.2 kJ mol^{-1} after 64 days of ageing in water at 100°C. The changes in activation energy will be used to make a life-time prediction of umbilical lines.

KEY WORDS: polyethylene; solvent; ageing

INTRODUCTION

Thermoplastic hoses have been used in umbilicals for over 25 years for control applications and to carry production service fluids from a control or service centre to sub-sea wellheads or subsea production centres. Umbilicals have an expected service life of around 20 years and it is vital that they withstand the harsh environmental conditions to which they are subjected, as well as sometimes carrying, highly aggressive, well service fluids. As oil and gas recovery moves into deeper waters, the installation of umbilicals becomes increasingly expensive. The durability of the fluid conduit materials of construction is therefore very important with the ever-increasing number of production service fluids, as the umbilicals should last for the duration of the design life.
The aim of this study is to improve the existing method of predicting the service life of thermoplastic hose fluid conduits by accelerated ageing studies.
Accelerated ageing studies usually involve heat-ageing tests, in which the material is tested at temperatures much higher than the actual service temperature. This will give results in a much shorter time and by extrapolating the data, the material's conditions at lower temperatures can be derived. This method is widely used to predict polymer properties [Braginskii, Dashevskaya and Peshkov, 1982; Bruggeman, Yang, Zaoutsos, Boulpaep, Dumortier and Cardon, 1998], but as Bright [1993] pointed out, many problems are connected with it.
The temperature ranges have to be sufficiently high to yield significant property changes, which can then be extrapolated. As a consequence the temperatures used often traverse at least one polymeric phase transition. Degradation mechanisms change with the polymer's physical state and therefore affect rate parameters representative of another physical state. The Arrhenius equation is commonly used to calculate the rate of relaxation within a polymer and monitor the change or the rate over time in accelerated ageing data. However, in the Arrhenius equation the rate is a function of temperature only and the activation energy of the degradation mechanism is to remain constant over the temperature range of evaluation and extrapolation. This means that this approximation is only valid for single relaxation processes that give a linear response.
An alternative is the Williams-Landel-Ferry (WLF) equation, which applies to all relaxation processes, but it is only applicable at temperatures above the glass transition (T_g) of a polymer.
In addition to studying the thermal ageing of the material, the effect of chemical degradation has also to be taken into account.
Chemicals cannot just alter a polymer's property through chemical degradation, however, but simple absorption of the fluid by the polymer can lead to its plasticisation and might change the latter's mechanical properties significantly.
In this study several techniques were used to analyse changes in the material's chemical and physical properties and make a connection between chemical and mechanical changes.

METHOD

Extruded PE samples were aged at 100°C under constant pressure (200 bar) in water and methanol and at 40°C and 70°C under constant and cyclic pressure (200 bar) in water, methanol and xylene. Samples were taken regularly and analysed by Dynamic Mechanical Thermal Analysis (DMTA), Differential Scanning Calorimetry (DSC) and tensile tests. The DSC data at 40°C and 70°C were taken from cyclic pressure tests, whereas all other results were taken from constant pressure tests. This was due to availability of the samples. At a later date the differences occurring due to constant and cyclic pressure will be investigated.
Gravimetric tests were conducted separately by immersing samples in